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RESEARCH MEMORANDUM

THERMAL RELATIONS FOR TWO-PHASE EXPANSION WITH PHASE EQUILIBRIUM AND EXAMPLE FOR COMBUSTION PRODUCTS OF BORON-CONTAINING FUEL

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NATIONAL ADVISORY COMMITTEE
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SUMMARY

Jet engine fuels containing boron form boric oxide (B_2O_3) when burned. This substance can exist both as a liquid and a vapor at high temperatures. If a portion of the B_2O_3 condenses during expansion, the performance of the engine can be affected appreciably. The physically possible effect of condensation on performance is often bracketed by assuming that expansion occurs either with no change in composition or with equilibrium condensation.

One method of calculating the isentropic expansion process is by means of equations relating pressure, temperature, and density. Commonly used equations from engineering thermodynamics relating these variables are not suited to the analysis of an isentropic process involving equilibrium condensation. This report presents equations relating temperature, pressure, and density for an isentropic process with equilibrium condensation.

The importance of using equations which properly describe this process is emphasized by a calculation discussed herein of the isentropic variation of pressure with temperature involving combustion products of boron. At the chosen condition, the coefficient for the isentropic variation of pressure with temperature was 5.8 with no phase change assumed and 12.9 with condensation assumed to occur.

A procedure is given for integrating the equations involving pressure, temperature, and density in order to analyze an expansion process. An example in the form of a problem concerning the use of ethyldecaborane in a ramjet engine serves to illustrate this procedure.

INTRODUCTION

The large heating values of boron-containing fuels offer the possibility of improvement in the flight range of air-breathing jet engines. The degree of improvement over hydrocarbon fuels depends in part both on the thermal properties of the combustion products and on the nature of

the expansion process. The boron-containing fuels differ from conventional fuels because they produce boric oxide (B_2O_3), which can exist simultaneously as a vapor and a liquid. If condensation of the oxide occurs during the expansion process, an appreciable effect upon thrust may be encountered under certain conditions.

The degree to which condensation occurs in actual expansion processes depends upon the rate of condensation relative to the time of expansion. In the absence of information on condensation rates it is customary to bracket the region of probable performance with calculations that assume either infinitely fast or infinitely slow condensation rates. These are designated respectively as expansion with equilibrium condensation and expansion with no condensation.

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Expansions with no condensation are readily handled and understood by means of elementary thermodynamic concepts. Expansions with equilibrium condensation are more difficult to handle. It is important that performance calculations involving the assumption of phase equilibrium be based upon correct equations and procedures.

The purpose of this report is to define certain properties for an expansion process involving combustion products with equilibrium condensation. These properties are (1) the variation of pressure with density at constant entropy $(\partial P/\partial \rho)_s$; (2) the variation of pressure with temperature at constant entropy $(\partial P/\partial T)_s$; (3) the variation of stream velocity at constant entropy $(dU)_s$. A numerical integration of these terms provides the pressure, temperature, density, velocity, and local Mach number at any point during the expansion. A procedure for integrating these terms is given, together with an example of the analysis of a specific expansion condition.

The equations and procedure herein omit the effect of dissociation of gases. Dissociative reactions generally assume importance only above 4000° R at pressures encountered in high-speed flight. For practically all conditions where boron-carbon-hydrogen fuels might be burned in air-breathing jet engines, saturation of the gases in the exhaust nozzle will not occur until a temperature less than 4000° R occurs.

Previous reports present other methods whereby the expansion process with phase equilibrium can be analyzed. Reference 1 contains a general procedure by which the nozzle outlet velocity can be obtained for specified nozzle inlet conditions and expansion ratio. Isentropic expansion can be considered for systems with compositions either frozen or in phase and chemical equilibrium. In addition, reference 1 presents a procedure for determining combustion temperatures which includes the effect of dissociation.

Because of the effort required in applying the procedures of reference 1 to specific performance calculations, the authors of reference 2 developed a simplified method for fuels containing boron, carbon, and hydrogen burned in air. The thermal properties for combustion products of certain stoichiometrically burned fuels are added to obtain properties for fuels containing boron, carbon, and hydrogen in any proportion and at any equivalence ratio. The properties are in tabular form and also in the form of pressure-enthalpy charts.

The charts of reference 2 include the effect of both vaporization and phase change. In regions where two phases are present, the charts can properly be used for the specific fuels and equivalence ratios for which they were calculated. The tables of reference 2 neglect dissociation of gases, but they can be used to include the effect of phase change. It is correct to add properties tabulated for combustion products of specific fuels to obtain the properties for any boron-carbon-hydrogen fuel when equilibrium phase change occurs. However, the determination of conditions at many points in the expansion process involves numerous trial and error calculations. Furthermore, the Mach number cannot be determined in a manner consistent with the assumed process of equilibrium condensation from data contained in the tables.

The equations and procedure in the present report provide a method alternative to those of references 1 and 2 for calculating the expansion process with equilibrium condensation of B_2O_3. In analyses where many points during the expansion are desired, this method may prove more convenient than the others. Moreover, the equations presented herein greatly aid in visualizing the effect of condensation on the expansion process.

DISCUSSION

Since the purpose of this report is to define thermal properties useful in analyzing an isentropic expansion process with two phases in equilibrium, these properties will first be listed. The isentropic variation of pressure with density is defined as

$$\left(\frac{\partial P}{\partial \rho}\right)_s = \gamma \frac{P}{\rho} \tag{1}$$

where

$$\gamma = \frac{1}{\frac{1}{1 - X_v} - \frac{\left[1 + \frac{X_v}{1 - X_v}\left(\frac{\Delta H_v}{RT}\right)\right]^2}{\left[\epsilon_{fr} + \frac{X_v}{1 - X_v}\left(\frac{\Delta H_v}{RT}\right)^2\right]}} \tag{2}$$

and

$$\varepsilon_{fr} = \left(\frac{c_p/c_v}{c_p/c_v - 1} \right)_{fr} \tag{3}$$

Symbols are defined in appendix A. The definitions of X_v and the last expression are described more explicitly in appendix B. The isentropic variation of pressure with temperature is

$$\left(\frac{\partial P}{\partial T} \right)_s = \varepsilon \frac{P}{T} \tag{4}$$

where

$$\varepsilon = \frac{\varepsilon_{fr} + \frac{X_v}{1 - X_v} \left(\frac{\Delta H_v}{RT} \right)^2}{1 + \frac{X_v}{1 - X_v} \left(\frac{\Delta H_v}{RT} \right)} \tag{5}$$

The differential form of the general energy equation for isentropic expansion can be expressed as

$$(UdU)_s = - \frac{RgJ}{m_m} dT = - \frac{RgJ}{m_m} d(\ln P) \tag{6}$$

The speed of sound is

$$c = \sqrt{\gamma P/\rho} \tag{7}$$

and Mach number is merely

$$M = U/c \tag{8}$$

Derivations of equations (2), (5), and (6) are collected in appendix C.

Equations (2) and (5) for γ and ε, respectively, are rigorous where condensation is the only change in composition. If the composition is assumed to be frozen during expansion so that no phase change occurs, those terms in equations (2) and (5) involving the heat of vaporization ΔH_v are zero. Equations (2) and (5) become the familiar expressions

$$\gamma = \gamma_{fr} = (c_p/c_v)_{fr} \tag{9}$$

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$$\varepsilon = \varepsilon_{fr} = \left(\frac{c_p/c_v}{c_p/c_v - 1} \right)_{fr} \tag{10}$$

from which

$$\varepsilon_{fr} = \frac{\gamma_{fr}}{\gamma_{fr} - 1} \tag{11}$$

is derived.

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When values of γ and ε computed for equilibrium phase change are compared to γ_{fr} and ε_{fr} for frozen composition, the marked effect of condensation on the flow process is emphasized. As an extreme example, consider the combustion products of boron at an equivalence ratio of 0.9, a pressure of 1 atmosphere, and a temperature of 3960° R (not the flame temperature). Assume that the combustion products are not dissociated at this temperature but that phase equilibrium exists. The ratio of gaseous to liquid B_2O_3 is then 2.102 at this condition. If expansion is assumed to occur with no condensation (frozen composition), γ_{fr} and ε_{fr} from equations (9) and (10) are 1.2083 and 5.802, respectively. If equilibrium condensation is assumed during expansion, γ and ε from equations (2) and (5) are 1.1234 and 12.939, respectively.

Values of γ and ε calculated from equations (2) and (5) include the effect of condensation, while the presence of dissociated gases is ignored. By means of the method presented in reference 1, both phase change and recombination of dissociated gases can be evaluated, although greater effort is involved than in the use of equations (2) and (5). For the example under consideration, γ is 1.1214 and ε is 13.091 if both phase change and recombination of dissociated products are included. These values agree reasonably well with the values neglecting dissociation calculated by use of equations (2) and (5). For the combustion products of most boron-containing fuels, saturated mixtures of B_2O_3 vapor to which equations (2) and (5) are applicable can exist only under conditions where dissociation is small.

By means of equations (2), (5), and (6), expansion processes involving equilibrium phase change can now be analyzed with the assumption that gaseous products are not dissociated. For small intervals of the expansion process, pressure and temperature do not change greatly. Both γ and ε can then be treated as constants in the interval. Equations (1), (4), and (6) can then be integrated for this small interval to give these equations:

$$P_z/P_y = (\rho_z/\rho_y)^{\gamma} \tag{12}$$

$$P_z/P_y = (T_z/T_y)^{\varepsilon} \tag{13}$$

$$U_z^2 - U_y^2 = \frac{R_g J \varepsilon}{m_m} (T_y - T_z) \tag{14}$$

These computations are repeated for the number of intervals into which the expansion is divided, with γ and ε recalculated for each interval.

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EXAMPLE

An example is included to illustrate the manner in which the equations developed herein are used to analyze a one-dimensional expansion with phase equilibrium. The example shows the effect which the assumption of equilibrium phase change has on the expansion process.

Consider the following problem: a ramjet engine burning ethyldecaborane fuel operates at 60,000 feet, a flight Mach number of 4.0, and an equivalence ratio of 0.6. Inlet and diffuser pressure recovery is 0.443, and combustion efficiency is 1.00. Combustor inlet Mach number is 0.175. Flameholder drag is neglected. The exhaust-nozzle outlet temperature and velocity are desired for isentropic expansion to ambient pressure with equilibrium condensation. Also desired are nozzle contours required for (1) constant change of velocity with distance along the nozzle and (2) constant change of Mach number with distance along the nozzle.

Charts and procedure discussed in appendix D were used to determine conditions at the combustor outlet. The combustion temperature and pressure were found to be 4400° R and 4.524 atmospheres, respectively (1 atm = 2116 lb/sq ft). Dissociation of gases was neglected in this calculation. Since no condensed B_2O_3 was present at the combustor outlet, the condition in the nozzle at which condensation became possible was found by a procedure in appendix D. For convenience in discussion, this condition where condensation can theoretically begin is referred to as nozzle station 1. Subsequent stations for the stepwise calculation in the condensed region are referred to as 2, 3, 4, and so forth. Eight steps were used to calculate that portion of the expansion process after the theoretical saturation point. The nozzle inlet was designated as station C, the nozzle outlet as station D. Nozzle station 9 thus corresponds to the nozzle outlet, station D.

Values for P, T, U, c, M, γ, and ε for station 1 onward are presented in table I. The detailed calculations shown in table II are discussed more fully in appendix D. By following the headings of table II the reader can make similar calculations for other conditions and other fuels containing boron, carbon, and hydrogen.

Observe in table I that two stations, 1 and 1(a), are shown to have the same condition of static temperature and pressure. The temperature at station 1 was assumed to be infinitesimally above the temperature where condensation starts in this particular case. That at station 1(a) was assumed to be infinitesimally below the condensation condition. Sharp discontinuities in γ and ε result because of the sudden appearance of terms containing ΔH_v in equations (2) and (5) with the onset of condensation. The stream properties P, T, and U are the same at stations 1 and 1(a). However, the sonic velocity and Mach number jump because of the discontinuity in γ with the onset of condensation.

Between stations 1 and 1(a) there is a 100-percent increase in ε for equilibrium condensation over the value for no condensation at the same temperatures. There is an 8-percent decrease in γ for the same circumstances.

From the data of table I were computed the nozzle contours required for (1) constant change of velocity with distance along the nozzle axis and (2) constant change of Mach number with distance. The nozzle was assumed to be of circular cross section and 2 feet long. The nozzle radius required to pass 1 pound of mixture per second is shown plotted against axial distance for both cases in figure 1. Also shown in figure 1 is the nozzle contour for constant increase of velocity with distance if no condensation were to occur.

For the case of constant Mach number increase a procedure in appendix D avoids a discontinuity in the nozzle contour between stations 1 and 1(a). Such a discontinuity would otherwise result from the sudden increase in γ caused by the onset of condensation. Between the nozzle inlet (station C) and station 1 the value of ε_{fr} used in computing stream velocity from equation (14) is assumed to be 5.15, while γ_{fr} is assumed to be 1.24 in equation (7) for the speed of sound. The flow areas and Mach numbers between station C and the saturation condition calculated using these values of γ_{fr} and ε_{fr} assume no dissociation of gases. Incorporating the effect of dissociation between these stations changes the flow areas and Mach numbers very slightly in this particular example.

Lewis Flight Propulsion Laboratory
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APPENDIX A

SYMBOLS

A	specific nozzle area, sq ft/(lb/sec)
a	constant in expression for molar entropy
C_P^o	constant-pressure specific heat of substance, Btu/(lb mole)(^oR)
c	local speed of sound, ft/sec
c_P	constant-pressure specific heat of combustion products at constant composition, Btu/(lb)(^oR)
c_V	constant-volume specific heat of combustion products at constant composition, Btu/(lb)(^oR)
g	gravitational constant, 32.17 ft/sec^2
H_T^o	total enthalpy of combustion-product constituent (sum of chemical energy and sensible enthalpy), Btu/lb mole
ΔH_V	heat of vaporization, Btu/lb mole
h	total enthalpy (sum of chemical energy and sensible enthalpy), Btu/lb
Δh_c	heat of combustion of fuel, Btu/lb
J	conversion factor, 778.16 ft-lb/Btu
l	distance along nozzle axis, ft
M	Mach number, ratio of stream velocity to local speed of sound
m	molecular weight, lb/lb mole
m_m	mean molecular weight of combustion products, lb/lb mole
n	number of moles
n'	number of moles of combustion-product constituent resulting from burning fuel stoichiometrically in 1 pound of air
P	static pressure of combustion products, atm (1 atm = 2116 lb/sq ft)

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p	partial pressure of combustion-product constituent, atm
R	gas constant, 1.98718 Btu/(lb mole)($^{\circ}$R)
S	entropy of substance, Btu/(lb mole)($^{\circ}$R)
s	entropy of mixture of materials, Btu/$^{\circ}$R
T	static temperature, $^{\circ}$R
U	axial stream velocity, ft/sec
V	volume of mixture of combustion products, cu ft
W	weight, lb
X	number of moles of constituent divided by total moles of gas and vapor
γ	coefficient for variation of pressure with density at constant entropy
ε	coefficient for variation of pressure with temperature at constant entropy
$\bar{\varepsilon}$	arithmetic average of ε over temperature interval
ρ	density, lb/cu ft
Φ	equivalence ratio, actual fuel-air ratio divided by stoichiometric fuel-air ratio

Subscripts:

a	air
B	combustor inlet
C	combustor outlet or nozzle inlet
c	condensed phase
D	nozzle outlet
f	fuel
fr	no change in composition (frozen composition)

g	noncondensing gases only, vapor of condensing material excluded
i	all gases, including vapor of condensing material
k	all materials, including condensed phase
P	constant pressure
s	constant entropy
st	stoichiometric
T	constant temperature
v	vapor phase of condensing material
y,z	adjacent stations in flow
α,β,λ	atoms of boron, hydrogen, and carbon, respectively, in fuel formula $B_\alpha H_\beta C_\lambda$
η=1,2,3	stations in nozzle after condensation begins

APPENDIX B

RELATIONS FOR ONE-DIMENSIONAL ISENTROPIC EXPANSION WITH NO CONDENSATION AND NO DISSOCIATION

This appendix discusses the definitions of γ and ε for the isentropic expansion of two-phase systems with no condensation. Similar material has been presented elsewhere (ref. 3), but the topic is discussed here because some of the terms derived are required in the analysis of equilibrium condensation in appendix C.

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Consider a mixture of ideal gases containing finely divided condensed material too large for Brownian motion. The ideal gas law applied to the gases in the mixture is

$$PV = RJT\Sigma n_i \tag{B1}$$

The density of the mixture including the condensed phase is

$$\rho = \Sigma n_k m_k / V \tag{B2}$$

provided the volume of the condensed phase is negligible compared to that of the gas. Substituting equation (B2) in equation (B1) gives

$$\frac{P}{\rho} = RJT \frac{\Sigma n_i}{\Sigma n_k m_k} \tag{B3}$$

The term $\Sigma n_k m_k / \Sigma n_i$ can be regarded as m_m, the mean molecular weight of the mixture of gases and condensed material, as contrasted with the mean molecular weight of the gases alone, which is defined as $\Sigma n_i m_i / \Sigma n_i$.

The derivative $(\partial P/\partial T)_s$ is found by considering the general expression for reversible entropy change

$$T\,ds = dh - \frac{V}{J}\,dP \tag{B4}$$

If composition is fixed (no condensation) and there is thermal equilibrium between particles and gas,

$$dh = \Sigma n_k (C_P^o)_k dT \tag{B5}$$

Set ds equal to zero. Then combine equations (B3), (B4), and (B5) to obtain

$$\left(\frac{\partial P}{\partial T}\right)_{s,fr} = \frac{P}{T}\frac{\Sigma n_k (C_P^o)_k}{R\Sigma n_i} \tag{B6}$$

Equation (B6) can be expressed somewhat differently. Let the mole fraction for all constituents including the condensed phase be defined as $X_k = n_k/\Sigma n_i$. The number of moles of condensed material is not included in the summation Σn_i. For this reason, $\Sigma X_k = 1 + X_c$. This convention, used throughout the remainder of this report, gives

$$\left(\frac{\partial P}{\partial T}\right)_{s,fr} = \frac{\Sigma X_k (C_P^o)_k}{R}\frac{P}{T} = \varepsilon_{fr}\frac{P}{T} \tag{B7}$$

The derivative $(\partial P/\partial \rho)_s$ can be found by differentiating the logarithm of equation (B3) with respect to density at constant entropy with $\Sigma n_k m_k$ constant for a given weight of mixture:

$$\left(\frac{\partial P}{\partial \rho}\right)_s = \frac{P}{\rho} + \frac{P}{T}\left(\frac{\partial T}{\partial P}\right)_s \left(\frac{\partial P}{\partial \rho}\right)_s + \frac{P}{\Sigma n_i}\left(\frac{\partial \Sigma n_i}{\partial \rho}\right)_s \tag{B8}$$

For frozen composition $(\partial \Sigma n_i/\partial \rho)_s$ is zero. Combining equations (B6) and (B8) gives

$$\left(\frac{\partial P}{\partial \rho}\right)_{s,fr} = \gamma_f \frac{P}{\rho} = \left[\frac{\Sigma n_k (C_P^o)_k}{\Sigma n_k (C_P^o)_k - R\Sigma n_i}\right]\frac{P}{\rho} \tag{B9}$$

Thus, for frozen composition

$$\gamma_{fr} = \frac{\Sigma n_k (C_P^o)_k / \Sigma n_k m_k}{[\Sigma n_k (C_P^o)_k / \Sigma n_k m_k] - R\Sigma n_i / \Sigma n_k m_k} \tag{B10}$$

The numerator of expression (B10) is c_p and the denominator is c_v for a unit weight of the mixture of gases and condensed material. The definition of γ for the case of frozen composition is thus extended by equation (B10) to include the situation of small particles in velocity and temperature equilibrium with the gas.

Equation (B10) expressed in terms of mole fraction is

$$\gamma_{fr} = \frac{\Sigma X_k (C_P^o)_k}{\Sigma X_k (C_P^o)_k - R} \tag{B11}$$

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Equations (B7) and (B11) can be combined to give

$$\varepsilon_{fr} = \frac{\gamma_{fr}}{\gamma_{fr} - 1} \tag{B12}$$

Only by specifying frozen composition is the relation between ε and γ obtained as given by equation (B12).

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APPENDIX C

RELATIONS FOR ONE-DIMENSIONAL ISENTROPIC EXPANSION WITH PHASE CHANGE OF ONE CONSTITUENT AND NO DISSOCIATION

In this appendix, equations (2), (5), and (6), for γ, ε, and dU, respectively, are derived. These expressions pertain to two-phase isentropic expansion with phase equilibrium.

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Derivation of ε

It is convenient to derive ε first. The result can then be used to find γ. For a fixed mass of material with gases behaving ideally,

$$s = \Sigma n_k S_k \tag{C1}$$

where the summation over k terms includes the condensed phase and its vapor as well as the noncondensing gases.

For the noncondensing gases and the vapor phase of the condensing material, collectively represented by the subscript i,

$$S_i = \int \frac{(C_P^o)_i}{T} dT - R \ln p_i + a_i \tag{C2}$$

For the condensed phase the entropy can be considered nearly independent of pressure. Hence (see ref. 4),

$$S_c = \int \frac{(C_P^o)_c}{T} dT + a_c \tag{C3}$$

In an isentropic process

$$ds = 0 = \Sigma n_k dS_k + \Sigma S_k dn_k \tag{C4}$$

Representing both S_k and n_k as functions of the temperature and pressure of the system yields

$$dS_k = \left(\frac{\partial S_k}{\partial P}\right)_T dP + \left(\frac{\partial S_k}{\partial T}\right)_P dT \tag{C5}$$

and

$$dn_k = \left(\frac{\partial n_k}{\partial P}\right)_T dP + \left(\frac{\partial n_k}{\partial T}\right)_P dT \tag{C6}$$

Combining equations (C4), (C5), and (C6) gives

$$\left(\frac{\partial P}{\partial T}\right)_s = - \frac{\Sigma n_k \left(\frac{\partial S_k}{\partial T}\right)_P + \Sigma S_k \left(\frac{\partial n_k}{\partial T}\right)_P}{\Sigma n_k \left(\frac{\partial S_k}{\partial P}\right)_T + \Sigma S_k \left(\frac{\partial n_k}{\partial P}\right)_T} \tag{C7}$$

If equation (C7) is to be valid, the particles must be in thermal equilibrium with the gas and vapor.

The derivatives are now evaluated. First find $\Sigma n_k (\partial S_k/\partial P)_T$. From equations (C2) and (C3)

$$\left(\frac{\partial S_i}{\partial P}\right)_T = - \frac{R}{p_i} \left(\frac{\partial p_i}{\partial P}\right)_T \tag{C8}$$

and $(\partial S_c/\partial P)_T = 0$. The partial pressure of a constituent in a mixture of ideal gases is

$$p_i = P n_i / \Sigma n_i \tag{C9}$$

where

$$\Sigma n_i = n_v + \Sigma n_g \tag{C10}$$

Assume that neither n_g nor Σn_g changes for the noncondensing gases. Differentiate the logarithm of equation (C9) for the vapor phase and combine the result with equation (C10) to obtain

$$\frac{1}{p_v} \left(\frac{\partial p_v}{\partial P}\right)_T = \frac{1}{P} + \frac{1}{n_v} \left(\frac{\partial n_v}{\partial P}\right)_T - \frac{1}{\Sigma n_i} \left(\frac{\partial n_v}{\partial P}\right)_T \tag{C11}$$

However, the partial pressure of a saturated vapor behaving as an ideal gas is a function of temperature only. The relation is known as the Clausius-Clapeyron equation (see ref. 4). In reference 4 it is shown that $(\partial p_v/\partial P)_T \to 0$ if the molar volume of the liquid becomes negligible compared to that of its vapor. Equation (C11) then gives

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$$\left(\frac{\partial n_v}{\partial P}\right)_T = - \frac{n_v}{P(1 - X_v)} \tag{C12}$$

where $X_v = n_v/\Sigma n_i$. For the noncondensing gases, differentiation of equation (C9) and substitution of equation (C12) yield

$$\frac{1}{p_g}\left(\frac{\partial p_g}{\partial P}\right)_T = \frac{1}{P} + \frac{X_v}{P(1 - X_v)} = \frac{1}{P(1 - X_v)} \tag{C13}$$

Finally, since $(\partial p_v/\partial P)_T$ is zero,

$$\Sigma n_k\left(\frac{\partial S_k}{\partial P}\right)_T = - \frac{R}{P}\frac{\Sigma n_g}{(1 - X_v)}$$

Substituting for Σn_g from equation (C10) results in

$$\Sigma n_k\left(\frac{\partial S_k}{\partial P}\right)_T = - \frac{R}{P}\Sigma n_i \tag{C14}$$

The term $\Sigma S_k(\partial n_k/\partial P)_T$ of equation (C7) is considered next. The mole numbers of only the condensed phase and its vapor are assumed to change. The relation between moles of liquid and moles of vapor is $dn_v = - dn_c$. Then

$$\Sigma S_k\left(\frac{\partial n_k}{\partial P}\right)_T = (S_v - S_c)\left(\frac{\partial n_v}{\partial P}\right)_T \tag{C15}$$

But

$$S_v - S_c = \Delta H_v/T \tag{C16}$$

Equation (C16), together with equation (C12), when substituted in equation (C17) gives

$$\Sigma S_k\left(\frac{\partial n_k}{\partial P}\right)_T = - \frac{n_v \Delta H_v}{PT(1 - X_v)}$$

which can be written

$$\Sigma S_k\left(\frac{\partial n_k}{\partial P}\right)_T = - \frac{Rn_v(\Delta H_v/RT)}{P(1 - X_v)} \tag{C17}$$

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The term $\Sigma S_k(\partial n_k/\partial T)_P$ of equation (C7) is now considered. Differentiate the logarithm of equation (C9) for the vapor phase with respect to temperature:

$$\frac{1}{p_v}\left(\frac{\partial p_v}{\partial T}\right)_P = \frac{1}{n_v}\left(\frac{\partial n_v}{\partial T}\right)_P - \frac{1}{\Sigma n_i}\left(\frac{\partial n_v}{\partial T}\right)_P \tag{C18}$$

This yields finally

$$\left(\frac{\partial n_v}{\partial T}\right)_P = \frac{n_v}{p_v(1 - X_v)}\left(\frac{\partial p_v}{\partial T}\right)_P \tag{C19}$$

For a liquid surface in equilibrium with its vapor, the Clausius-Clapeyron equation is

$$\frac{dp_v}{dT} = \frac{p_v \Delta H_v}{RT^2} \tag{C20}$$

if the molar volume of the liquid is negligible compared to that of its vapor (see ref. 4). This expression is applicable to vapors behaving as ideal gases. If the radii of the liquid surfaces are not too small, the value of ΔH_v can be taken as that of a flat liquid surface. For instance, the surface energy of a drop as small as 2.2×10^{-6} centimeter is negligible (ref. 5). The ratio of vapor pressures of the small drop and the flat liquid is a function of surface energy of the small drop (ref. 4). Therefore particles as small as 2.2×10^{-6} centimeter have nearly the same vapor pressure as the flat surface. Substituting equation (C20) in equation (C19) results in

$$\left(\frac{\partial n_v}{\partial T}\right)_P = \frac{n_v(\Delta H_v/RT)}{T(1 - X_v)} \tag{C21}$$

Because only n_v and n_c change,

$$\Sigma S_k\left(\frac{\partial n_k}{\partial T}\right)_P = (S_v - S_c)\left(\frac{\partial n_v}{\partial T}\right)_P \tag{C22}$$

Substitution of equations (C16) and (C21) in equation (C22) gives

$$\Sigma S_k\left(\frac{\partial n_k}{\partial T}\right)_P = \frac{R n_v(\Delta H_v/RT)^2}{T(1 - X_v)} \tag{C23}$$

The term $\Sigma n_k(\partial S_k/\partial T)_P$ of equation (C7) can now be found. From equations (C2) and (C3),

$$\left.\begin{aligned}\left(\frac{\partial S_i}{\partial T}\right)_P &= (C_P^o)_i/T - \frac{R}{p_i}\left(\frac{\partial p_i}{\partial T}\right)_P \\ \text{and} \\ \left(\frac{\partial S_c}{\partial T}\right)_P &= (C_P^o)_c/T\end{aligned}\right\} \tag{C24}$$

for any constituent. From equation (C9)

$$\frac{1}{p_g}\left(\frac{\partial p_g}{\partial T}\right)_P = -\frac{1}{\Sigma n_i}\left(\frac{\partial \Sigma n_i}{\partial T}\right)_P = -\frac{1}{\Sigma n_i}\left(\frac{\partial n_v}{\partial T}\right)_P$$

for noncondensing gases. This expression, together with equation (C18) and equations (C24), upon summation yields

$$\Sigma n_k\left(\frac{\partial S_k}{\partial T}\right)_P = \Sigma n_k (C_P^o)_k/T \tag{C25}$$

Substituting equations (C14), (C17), (C23), and (C25) in equation (C7) yields

$$\left(\frac{\partial P}{\partial T}\right)_s = \frac{\dfrac{\Sigma n_k (C_P^o)_k}{T} + \dfrac{R n_v (\Delta H_v/RT)^2}{T(1 - X_v)}}{\dfrac{R}{P}\Sigma n_i + \dfrac{R n_v (\Delta H_v/RT)}{P(1 - X_v)}}$$

Let $X_k = n_k/\Sigma n_i$ for any constituent including the condensed particles; then

$$\left(\frac{\partial P}{\partial T}\right)_s = \frac{P}{T}\left[\frac{\frac{1}{R}\Sigma X_k (C_P^o)_k + \dfrac{X_v}{1 - X_v}(\Delta H_v/RT)^2}{1 + \dfrac{X_v}{1 - X_v}(\Delta H_v/RT)}\right] \tag{C26}$$

In appendix B it is shown that if the composition of a mixture of gases and condensed particles is frozen (no change in composition)

$$\varepsilon_{fr} = \frac{\gamma_{fr}}{\gamma_{fr} - 1} = \Sigma X_k (C_P^o)_k/R$$

Rewrite equation (C26) as

$$\varepsilon = \left(\frac{\partial P}{\partial T}\right)_s \frac{T}{P} = \frac{\varepsilon_{fr} + \frac{X_v}{1 - X_v}\left(\Delta H_v/RT\right)^2}{1 + \frac{X_v}{1 - X_v}\left(\Delta H_v/RT\right)} \tag{5}$$

Observe that ε_{fr} in equation (5) must be evaluated by insertion of those values of the X_k's required for phase equilibrium at the temperature and pressure in question.

Equation (5) was derived on the assumption that the mixture was saturated so that B_2O_3 condensed. If the mixture is superheated or if expansion is frozen, no B_2O_3 condenses, and the heat of vaporization is not recovered. Equation (10) in the DISCUSSION results.

Derivation of γ

Consider equation (B8), the differential form of the ideal gas law:

$$\left(\frac{\partial P}{\partial \rho}\right)_s = \frac{P}{\rho} + \frac{P}{T}\left(\frac{\partial T}{\partial \rho}\right)_s + \frac{P}{\Sigma n_i}\left(\frac{\partial \Sigma n_i}{\partial \rho}\right)_s \tag{B8}$$

From equation (C10) write the last derivative in equation (B4) as

$$\left(\frac{\partial \Sigma n_i}{\partial \rho}\right)_s = \left(\frac{\partial n_v}{\partial P}\right)_s \left(\frac{\partial P}{\partial \rho}\right)_s \tag{C27}$$

Since $n_v = n_v(T,P)$,

$$\left(\frac{\partial n_v}{\partial P}\right)_s = \left(\frac{\partial n_v}{\partial P}\right)_T + \left(\frac{\partial n_v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_s \tag{C28}$$

Now, $(\partial P/\partial T)_s$ has been evaluated in equations (C26) and (5). It can be expressed as $(\partial P/\partial T)_s = \varepsilon P/T$ and the other derivatives of equation (C27) are given by equations (C12) and (C21). With these substitutions equation (C27) becomes

$$\left(\frac{\partial \Sigma n_i}{\partial \rho}\right)_s = \left[\frac{n_v(\Delta H_v/RT)}{P\varepsilon(1 - X_v)} - \frac{n_v}{P(1 - X_v)}\right]\left(\frac{\partial P}{\partial \rho}\right)_s \tag{C29}$$

Also,

$$\left(\frac{\partial T}{\partial \rho}\right)_s = \left(\frac{\partial T}{\partial P}\right)_s \left(\frac{\partial P}{\partial \rho}\right)_s$$

$$= \frac{T}{P\varepsilon}\left(\frac{\partial P}{\partial \rho}\right)_s \tag{C30}$$

Substituting equations (C29) and (C30) into equation (B8) and solving for $(\partial P/\partial \rho)_s$ gives

$$\left(\frac{\partial P}{\partial \rho}\right)_s = \frac{P}{\rho\left\{\frac{X_v}{1 - X_v} - \frac{1}{\varepsilon}\left[1 + \frac{X_v}{1 - X_v}\left(\frac{\Delta H_v}{RT}\right)\right] + 1\right\}} \tag{C31}$$

Eliminating ε by means of equation (5) gives

$$\left(\frac{\partial P}{\partial \rho}\right)_s = \frac{P}{\rho\left\{\frac{1}{1 - X_v} - \frac{\left[1 + \frac{X_v}{1 - X_v}\left(\frac{\Delta H_v}{RT}\right)\right]^2}{\left[\varepsilon_{fr} + \frac{X_v}{1 - X_v}\left(\frac{\Delta H_v}{RT}\right)^2\right]}\right\}} \tag{C32}$$

Finally

$$\gamma = \frac{\rho}{P}\left(\frac{\partial P}{\partial \rho}\right)_s = \frac{1}{\frac{1}{1 - X_v} - \frac{1}{\varepsilon}\left[1 + \frac{X_v}{1 - X_v}\left(\frac{\Delta H_v}{RT}\right)^2\right]} \tag{C33}$$

or

$$\gamma = \frac{1}{\frac{1}{1 - X_v} - \frac{\left[1 + \frac{X_v}{1 - X_v}\left(\frac{\Delta H_v}{RT}\right)\right]^2}{\left[\varepsilon_{fr} + \frac{X_v}{1 - X_v}\left(\frac{\Delta H_v}{RT}\right)^2\right]}} \tag{C33a}$$

The speed of sound in a region of phase change is then

$$c^2 = g\gamma\frac{P}{\rho} \tag{C34}$$

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Equation (C33) was derived by assuming that the B_2O_3 present condenses. If the mixture is superheated or if expansion is frozen, the terms $X_v/(1 - X_v)$ and $X_v\Delta H_v/RT(1 - X_v)$ in equation (C31) both vanish, since they result only from considering condensation. Equation (9) in the DISCUSSION then replaces equation (C33).

Differential Form of General Energy Equation

For an adiabatic process the general energy equation is

$$(U^2/2gJ) + (h/\Sigma n_k m_k) = \text{Constant} \tag{C35}$$

This can be differentiated to give

$$\frac{UdU}{gJ} + dh = 0 \tag{C36}$$

For an isentropic process, equations (B1) and (B4) give

$$\left(\frac{\partial h}{\partial P}\right)_s = \frac{RT\Sigma n_i}{P} \tag{C37}$$

Combining equations (C36) and (C37) gives

$$(UdU)_s = -\frac{gJ}{\Sigma n_k m_k}\left(\frac{\partial h}{\partial P}\right)_s dP = -gJRT\frac{\Sigma n_i}{\Sigma n_k m_k}\frac{dP}{P} \tag{C38}$$

But if m_m is defined as $\Sigma n_k m_k/\Sigma n_i$, equation (C38) becomes

$$(UdU)_s = -\frac{gJRT}{m_m} d(\ln P) \tag{C39}$$

Another form of this expression results from combining equation (C39) with equation (4):

$$(UdU)_s = -\frac{gJR\varepsilon}{m_m} dT \tag{C40}$$

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APPENDIX D

CALCULATION OF THE EXAMPLE

The calculation of the example consists of three parts. First, the combustor outlet conditions are determined. Second, the conditions in the nozzle at the theoretical saturation point are found. Third, the conditions through the remainder of the nozzle with equilibrium condensation are determined by a series of stepwise calculations based upon the equations developed herein.

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Combustor Outlet Conditions

The composition of the burned mixture, neglecting dissociation, is found as follows. The chemical formula of a fuel or mixture of fuels containing boron, carbon, and hydrogen can be represented as $B_\alpha H_\beta C_\lambda$, where α, β, and λ are integers or decimals. The atom fractions are then: for boron, $\alpha/(\alpha + \beta + \lambda)$; for hydrogen, $\beta/(\alpha + \beta + \lambda)$; for carbon, $\lambda/(\alpha + \beta + \lambda)$. These atomic ratios and the triangular chart of figure 2 are used to find the moles $n'_{B_2O_3}$ of B_2O_3, n'_{H_2O} of H_2O, and n'_{CO_2} of CO_2 formed by burning the fuel stoichiometrically in 1 pound of air. The composition for all equivalence ratios less than stoichiometric is then

$\Phi n'_{B_2O_3}$ moles B_2O_3/lb air

$\Phi n'_{H_2O}$ moles H_2O/lb air

$\Phi n'_{CO_2}$ moles CO_2/lb air

$0.00726(1-\Phi)$ moles O_2/lb air

0.02740 moles N_2/lb air

The stoichiometric fuel-air ratio used in computing Φ can be found by means of the atom fraction and figure 3.

For ethyldecaborane ($B_{10}C_2H_{18}$), the fuel considered in the example, the atom ratios are 0.333 for boron, 0.600 for hydrogen, and 0.067 for carbon. From figure 2 the stoichiometric mole numbers are found to be: $n'_{B_2O_3}$, 0.00259; n'_{H_2O}, 0.00466; and n'_{CO_2}, 0.00103. From figure 3 the stoichiometric fuel-air ratio is found to be 0.0778.

If the combustion temperature is less than the saturation temperature for B_2O_3 vapor, both condensed and gaseous B_2O_3 will be present. The criterion for the presence of the condensed phase is as follows:

$$n'_{B_2O_3} P/\Sigma n_k \geq p_v \tag{D1}$$

where

$$\Sigma n_k = \Phi(n'_{B_2O_3} + n'_{H_2O} + n'_{CO_2}) + 0.00726\ (1 - \Phi) + 0.02740 \tag{D2}$$

The vapor pressure is plotted against temperature in figure 4. If inequality (D1) indicates no condensed material, the amount of B_2O_3 vapor is merely

$$n_v = \Phi n'_{B_2O_3} \text{ moles/lb air} \tag{D3}$$

If the inequality indicates condensed material, the amount of B_2O_3 vapor is

$$n_v = \frac{p_v \Sigma n_g}{P - p_v} \tag{D4}$$

where

$$\Sigma n_g = \Sigma n_k - \Phi n'_{B_2O_3} \tag{D5}$$

and the amount of condensed B_2O_3 is merely

$$n_c = \Phi n'_{B_2O_3} - n_v \tag{D6}$$

The amount of noncondensing gases and B_2O_3 vapor is

$$\Sigma n_i = \Sigma n_g + n_v \tag{D7}$$

The total enthalpy of the burned mixture for a fuel containing boron, carbon, and hydrogen is then

$$\left(1 + \frac{W_f}{W_a}\right) h_C = n_c (H_T^o)_{B_2O_3,c} + n_v (H_T^o)_{B_2O_3,v} + \Phi n'_{H_2O} (H_T^o)_{H_2O} + \Phi n'_{CO_2} (H_T^o)_{CO_2} +$$

$$0.00726(1 - \Phi)(H_T^o)_{O_2} + 0.02740(H_T^o)_{N_2} \text{ Btu/lb air} \tag{D8}$$

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Total enthalpies of the constituents are plotted in figure 5. They include chemical energy. Data for B_2O_3 are from reference 6, while data for the other materials are from reference 1.

Conservation of energy across the combustor is expressed as

$$\left(h_a + \frac{W_f}{W_a} h_f\right)_B + \frac{U_B^2}{2gJ} = \left(1 + \frac{W_f}{W_a}\right)\left(h_C + \frac{U_C^2}{2gJ}\right) \qquad (D9)$$

Enthalpy of air is given in figure 6. Enthalpies of some fuels of interest taken from reference 2 are as follows:

Fuel	Formula	Phase	Temperature, $^\circ R$	Assigned enthalpy, h_f, Btu/lb
Boron	B	Crystal	--------	28,843
Diborane	B_2H_6	Gas	536.7	36,575
Ethyldecaborane	$B_{10}C_2H_{18}$	Liquid	536.7	36,263
Hydrocarbon fuel	C_xH_{2x}	Liquid		20,000
Pentaborane	B_5H_9	Liquid	536.7	33,828

Enthalpies of other fuels containing boron, carbon, and hydrogen in known proportions and having experimentally determined or empirically calculated heats of combustion can be found from the equation

$$h_f = \Delta h_c + \frac{1}{\left(\frac{W_f}{W_a}\right)_{st}}\left[(n'H_T^\circ)_{B_2O_3} + (n'H_T^\circ)_{H_2O} + (n'H_T^\circ)_{CO_2} - 0.00726(H_T^\circ)_{O_2}\right]$$

For heats of combustion determined at 298.16° K (536.7° R), $(H_T^\circ)_{O_2}$ is 24.642 Btu/lb mole, $(H_T^\circ)_{CO_2}$ is 4.026 Btu/lb mole, $(H_T^\circ)_{B_2O_3(crystal)}$ is 91.605 Btu/lb mole, and $(H_T^\circ)_{H_2O(vapor)}$ is 24.642 Btu/lb mole.

Combustion pressure P_C and velocity U_C required to evaluate expressions (D1), (D3), and (D9) are found by means of the momentum equation

$$\frac{U_C}{U_B}\frac{\left[1 + \frac{U_B^2}{gJ}\left(\frac{m_a}{RT}\right)_B\right]}{\left[1 + \frac{U_C^2}{gJ}\left(\frac{m_m}{RT}\right)_C\right]} = \left(1 + \frac{W_f}{W_a}\right)\frac{\left(\frac{RT}{m_m}\right)_C}{\left(\frac{RT}{m_a}\right)_B} \qquad (D10)$$

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and the continuity equation

$$\frac{P_B''}{P_B}\left(1 + \frac{W_f}{W_a}\right) P_B U_B \left(\frac{m_a}{RT}\right)_B = P_C U_C \left(\frac{m_m}{RT}\right)_C \qquad (D11)$$

where the static-pressure loss due to flameholder and combustor wall friction is represented by the ratio P_B''/P_B. The mean molecular weight m_m of the combustion products at station C can be expressed as

$$m_{m,c} = 69.64(X_c + X_v) + 18.016\, X_{H_2O} + 44.01\, X_{CO_2} + 32X_{O_2} + 28.016\, X_{N_2} \qquad (D12)$$

Also, $(R/m_a)_B$ is 0.06888 for the air composition assumed herein.

The determination of the combustion temperature requires that equations (D9), (D10), and (D11) be satisfied. Furthermore, if inequality (D1) shows the presence of condensed B_2O_3, the proper amounts of n_c and n_v determined from equations (D4), (D5), and (D6) must be used in equation (D9). The solution for a single combustion temperature may require several iterations.

For the example being considered the combustor inlet temperature T_B was found to be 1590° R, while the inlet pressure was 4.747 atmospheres. By iteration of equations (D9), (D10), and (D11) the flame temperature T_C was found to be 4400° R neglecting dissociation. Velocity U_C was 980 feet per second, and pressure P_C was 4.524 atmospheres. Since inequality (D1) revealed that no condensed B_2O_3 was present, the saturation condition for B_2O_3 may be reached in the expansion process.

Conditions in Nozzle at Saturation

The pressure and temperature at the saturation point can be found from conditions at the combustor outlet. For the combustion temperature T_C and the parameter $\Phi n'_{B_2O_3} P_C/\Sigma n_k$, the ratio P_1/P_C is read from figure 7. The ratio T_1/T_C can be calculated from equation (13) using an ε of 5.15. The subscript 1 refers to the condition where saturation is reached. For the example herein $\Phi n'_{B_2O_3} P_C/\Sigma n_k$ is 0.199. This value, together with the combustion temperature of 4400° R, determines a P_1/P_C of 0.637 and a T_1/T_C of 0.916. Thus P_1 and T_1 are 2.885 atmospheres and 4032° R, respectively.

If the inequality (D1) shows the presence of condensed B_2O_3 at the combustor outlet conditions, figure 7 cannot be used. The derivation of the equation from which figure 7 is constructed appears at the end of this appendix.

Expansion with Phase Equilibrium

The equations developed in appendixes B and C are used to calculate conditions through the region of phase change in the nozzle. The detailed calculation procedure is illustrated in table II. The reader, by following the headings of table II, can make similar calculations for isentropic expansion with phase change. Alternate procedures are provided in table II for those cases where the mixture is superheated and those cases where the mixture is saturated. A test is provided for determining which case is present at any condition.

At the precise point where the condensation can commence, the computation can be made either way. The temperature and pressure in rows 1 and 1(a) of table II for the example are such that the test for condensed B_2O_3 shows this to be the condition where saturation is reached. This is a consequence of having used figure 7 to determine the saturation point for the example. Row 1 was worked assuming that the test for condensed material showed the mixture to be very slightly superheated. Row 1(a), for the same temperature and pressure as row 1, was worked with the assumption that the mixture was very slightly below the point of saturation. Column 15 of table II can be expressed as

$$\frac{X_k(C_P^o)_k}{R} = \frac{1}{R}\Big[X_v(C_P^o)_{B_2O_3,v} + X_c(C_P^o)_{B_2O_3,c} + X_{H_2O}(C_P^o)_{H_2O} + X_{CO_2}(C_P^o)_{CO_2} + X_{O_2}(C_P^o)_{O_2} + X_{N_2}(C_P^o)_{N_2}\Big] \qquad (D13)$$

The variation of the constant-pressure specific heats C_P^o with temperature for the products is given in figure 8. Inspection of column 15 in table II shows that summation (D13) could have been approximated by a value of about 5 over the entire range of conditions in the table. Values of $\Delta H_v/RT$ for B_2O_3, column 16, are shown in figure 9 as a function of temperature.

Calculation of Nozzle Contours

Consider the case of constant change of velocity with Mach number. The distance from the nozzle inlet to any station η for a nozzle 2 feet in length is

$$l_\eta = \frac{2}{U_D - U_C}(U_\eta - U_C)$$

For the case of constant change of Mach number with length there is a discontinuity in Mach number at the point of condensation. This is circumvented by calculating the distance l_η as follows

$$l_\eta = \frac{2}{M_D - M_{1(a)} + M_1 - M_C}(M_\eta - M_C)$$

Derivation of Equation Used to Construct Figure 7

If inequality (D1) shows no condensed B_2O_3 at the combustor outlet, the partial pressure of B_2O_3 in the nozzle can be represented at any point down to the saturation condition by

$$\frac{\Phi n'_{B_2O_3} P}{\Sigma n_k}$$

At the saturation point (station 1) the partial pressure is equal to the partial pressure of the vapor in equilibrium with the condensed phase. The latter can be represented approximately over quite a range of temperature by

$$e^{14.87 - 68,300/T_1}$$

Equating these expressions for the saturation point gives

$$\frac{\Phi n'_{B_2O_3} P_1}{n_k} = e^{14.87 - 68,300/T_1} \tag{D14}$$

Assume that composition does not change between station C and station 1. It is then possible to define a mean $\bar{\varepsilon}_{fr}$ for this interval such that

$$T_C/T_1 = (P_C/P_1)^{1/\bar{\varepsilon}_{fr}}$$

Equation (D14) can then be rearranged as

$$\frac{\Phi n'_{B_2O_3} P_C}{n_k} = \frac{P_C}{P_1} e^{14.87 - \frac{68,300}{T_C}\left(\frac{P_C}{P_1}\right)^{1/\bar{\varepsilon}_{fr}}} \tag{D15}$$

A constant value for $\bar{\varepsilon}_{fr}$ of 5.15 was chosen in constructing figure 7.

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TABLE I. - PROPERTIES OF EXPANDING COMBUSTION PRODUCTS AT POINTS WITHIN REGION OF BORIC OXIDE (B_2O_3) CONDENSATION

Nozzle station, η	Static pressure, P, atm	Static temperature, T, ^{o}R	Velocity, U, ft/sec	Speed of sound, c, ft/sec	Mach number, M	Coefficient of pressure-density variation, γ	Coefficient of pressure-temperature variation, ε
1	2.885	4032	2705	2910	0.9296	1.253	4.947
1(a)	2.885	4032	2705	2787	.9706	1.149	10.048
2	1.817	3851	3634	2709	1.341	1.151	9.584
3	1.144	3670	4325	2636	1.641	1.156	8.978
4	.720	3486	4880	2568	1.900	1.166	8.090
5	.454	3293	5341	2507	2.130	1.183	7.045
6	.286	3084	5738	2445	2.347	1.207	6.071
7	.180	2858	6090	2378	2.565	1.230	5.408
8	.113	2622	6409	2287	2.802	1.244	5.115
[a]9	.0712	2396	6689	2191	3.053	1.250	4.993

[a]Nozzle outlet, station D.

TABLE II. - CALCULATION PROCEDURE FOR ISENTROPIC EXPANSION PROCESS WITH EQUILIBRIUM CONDENSATION

Nozzle station, η	1	2	3	4	5	6	7	8	6	8	9	10
	P, atm	T, $(2)_{\eta-1}\left[\frac{(1)_\eta}{(1)_{\eta-1}}\right]^{\frac{1}{(19)_{\eta-1}}}$, °R	$\frac{\Phi n_{B_2O_3}}{\Sigma n_k}$	p_v (fig. 4), atm	If (3) ≥ (4)				If (3) ≤ (4)		X_v, (6)/(8)	X_c, (7)/(8)
					P - p_v, (1)-(4)	n_v, $\frac{(4)\Sigma n_g}{(5)}$	n_c, $\Phi n'_{B_2O_3}$ -(6)	Σn_1, (6)+Σn_g	n_v, $\Phi n'_{B_2O_3}$	Σn_1, (6)+Σn_g		
1	2.885	4032	0.127	0.127	--------	----------	----------	----------	0.00155	0.03527	0.0439	0
1(a)	2.885	4032	.127	.127	2.758	0.00155	0	0.03527	-------	-------	.0439	0
2	1.817	3851	.080	.058	1.759	.00111	.00044	.03483	-------	-------	.0319	.0126
3	1.144	3670	.050	.0245	1.1195	.00074	.00081	.03446	-------	-------	.0215	.0235
4	.720	3486	.0316	.00925	.71075	.00044	.00111	.03416	-------	-------	.0129	.0325
5	.454	3293	.0199	.00289	.45111	.00022	.00133	.03394	-------	-------	.0065	.0392
6	.286	3084	.0126	.000700	.28530	.000083	.00147	.03380	-------	-------	.0025	.0435
7	.180	2858	.0079	.000115	.17988	.000022	.00153	.03374	-------	-------	.000652	.0453
8	.113	2622	.0050	.0000124	.11299	.0000037	.001546	.033724	-------	-------	.000110	.0458
9	.0712	2396	.00312	.00000097	.071199	.00000046	.0015495	.0337205	-------	-------	.00001	.0460

Nozzle station, η	11	12	13	14	15	16	17	18	19	19	20	21	22	22	
	X_{H_2O}, $\frac{\Phi n'_{H_2O}}{(8)}$	X_{CO_2}, $\frac{\Phi n'_{CO_2}}{(8)}$	X_{O_2}, $\frac{1-\Phi}{(8)}$	X_{N_2}, $\frac{0.02740}{(8)}$	$\frac{\Sigma X_k C^o_{P,k}}{R}$	If (3) ≥ (4)				If (3)<(4)	If (3) ≥ (4)				If (3)<(4)
						$\frac{\Delta H_v}{RT}$ (fig. 9)	1 - X_v, 1 - (9)	$\frac{(9)(16)}{(17)}$	ε, $\frac{(15)+(16)(18)}{1+(18)}$	ε (a)	$\frac{1}{1-X_v}$, 1/(17)	$\frac{1+(18)}{(19)}$	γ, $\frac{1}{(20)-(21)}$	γ, $\frac{(15)}{(15)-1}$	
1	0.0794	0.0176	0.0822	0.7768	4.947	-----	-------	-------	------	4.947	------	------	-----	1.253	
1(a)	.0794	.0176	.0822	.7768	4.947	16.7	0.9561	0.7668	10.048		1.0459	0.1758	1.149	-----	
2	.0803	.0177	.0834	.7867	5.020	17.5	.9681	.5766	9.584		1.0330	.1645	1.151	-----	
3	.0811	.0179	.0843	.7951	5.077	18.55	.9785	.4076	8.978		1.0220	.1568	1.156	-----	
4	.0819	.0181	.0850	.8021	5.121	19.65	.9871	.2568	8.090		1.0130	.1554	1.166	-----	
5	.0824	.0182	.0856	.8073	5.139	20.95	.9935	.1371	7.045		1.0065	.1614	1.183	-----	
6	.0827	.0183	.0859	.8106	5.135	22.60	.9975	.0566	6.071		1.0025	.1740	1.207	-----	
7	.0829	.0183	.0861	.8121	5.101	24.60	.99935	.0160	5.408		1.0006	.1879	1.230	-----	
8	.0829	.0183	.0861	.8125	5.050	27.10	.99989	.00298	5.115		1.0001	.1961	1.244	-----	
9	.0829	.0183	.0861	.8126	4.985	29.95	.99999	.00030	4.993		1.0	.2003	1.250	-----	

Nozzle station, η	23	24 [a]	25	26	27	28	29	30	31	32
	m_m, $\Sigma X_k m_k$	ρ, $\frac{(1)(23)}{0.7302(2)}$, lb/cu ft	$\bar{\varepsilon}$, $\frac{(19)_{\eta-1}+(19)_\eta}{2}$	ΔT, $(2)_{\eta-1}-(2)_\eta$	$\frac{99,492(25)(26)}{(23)}$	$(27)_\eta+(28)_{\eta-1}$	U, $\sqrt{(28)}$, ft/sec	A, $\frac{1}{(24)(29)}$, $\frac{\text{sq ft}}{(\text{lb/sec})}$	c, $\sqrt{\frac{68,079(1)(22)}{(24)}}$, $\frac{\text{ft}}{\text{sec}}$	M, $\frac{(29)}{(31)}$
1	29.66	0.02906	------	---	----------	7.31769×10^6	2705.1	0.01272	2910	0.9296
1(a)	29.66	.02906	------	---	----------	7.31769	2705.1	.01272	2787	.9706
2	30.03	.01940	9.8160	181	5.8879×10^6	13.2056	3634.0	.01418	2709	1.341
3	30.36	.01296	9.281	181	5.5024	18.7080	4325.3	.01784	2636	1.641
4	30.63	.008664	8.534	184	5.1018	23.8098	4879.5	.02365	2568	1.900
5	30.82	.005819	7.5675	193	4.7143	28.5241	5340.8	.03218	2507	2.130
6	30.96	.003932	6.558	209	4.4044	32.9285	5738	.04433	2445	2.347
7	31.01	.002675	5.7395	226	4.1611	37.0896	6090	.06139	2374	2.565
8	31.01	.001830	5.2615	236	3.9833	41.0729	6409	.08525	2287	2.802
9	31.02	.001262	5.054	226	3.6629	44.7358	6689	.11846	2191	3.053

[a] Values same as in column 15.

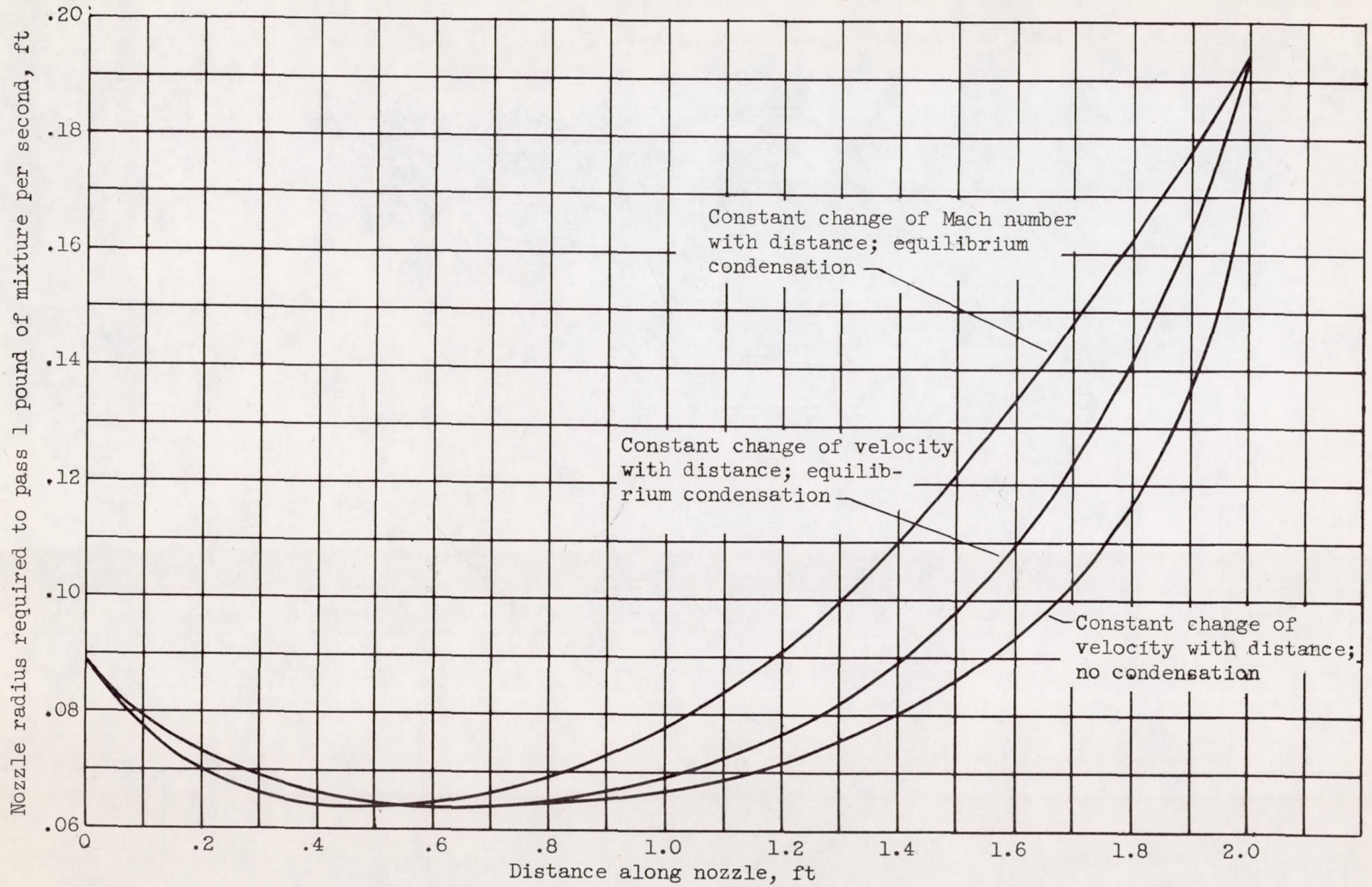


Figure 1. - Nozzle contour for constant change of velocity with distance and for constant change of Mach number with distance. Ramjet engine at 60,000 feet and flight Mach number of 4.0; ethyldecaborane fuel; equivalence ratio, 0.6.

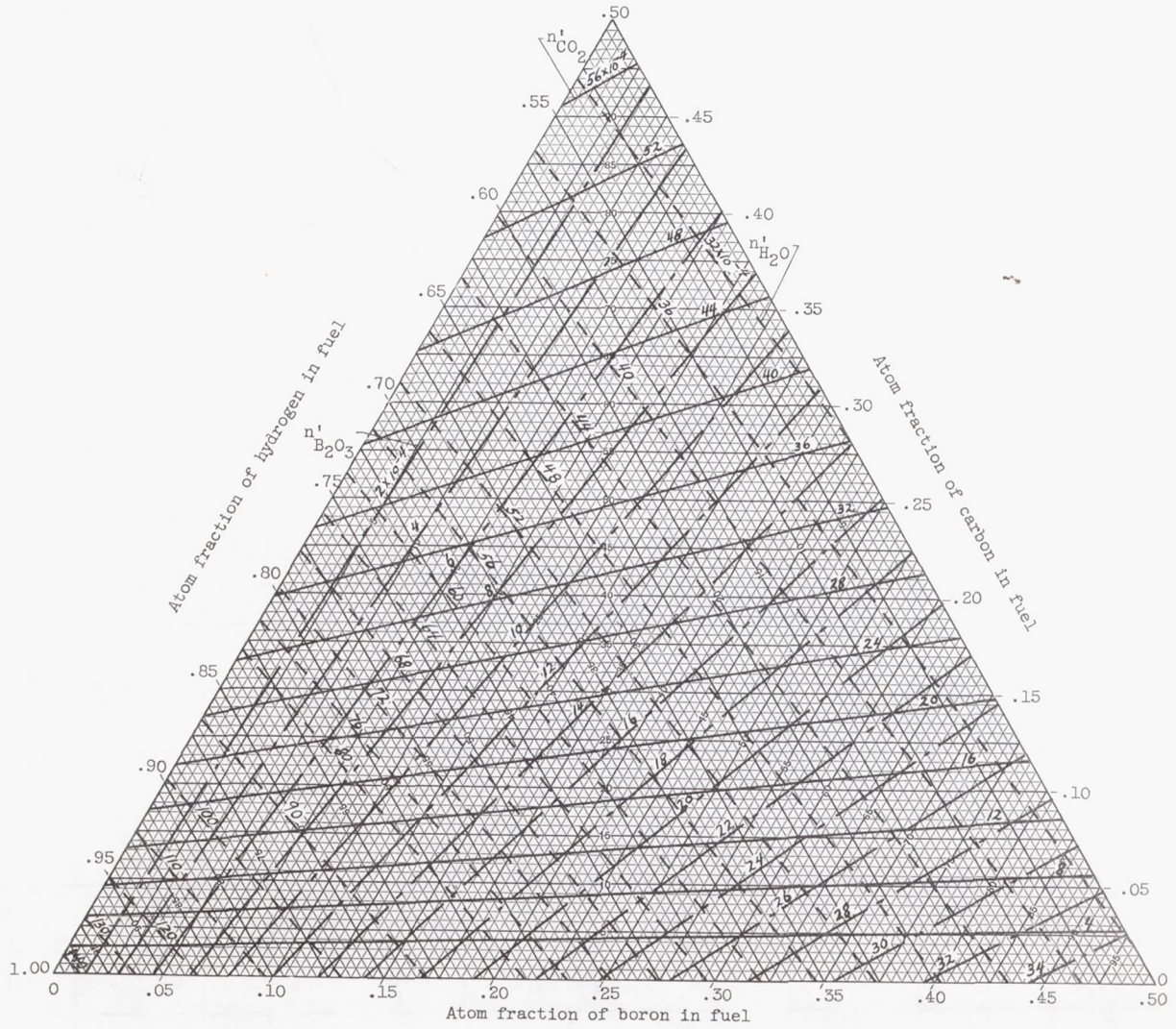


Figure 2. - Moles of boric oxide, carbon dioxide, and water formed by stoichiometric burning of fuel in 1 pound of air.

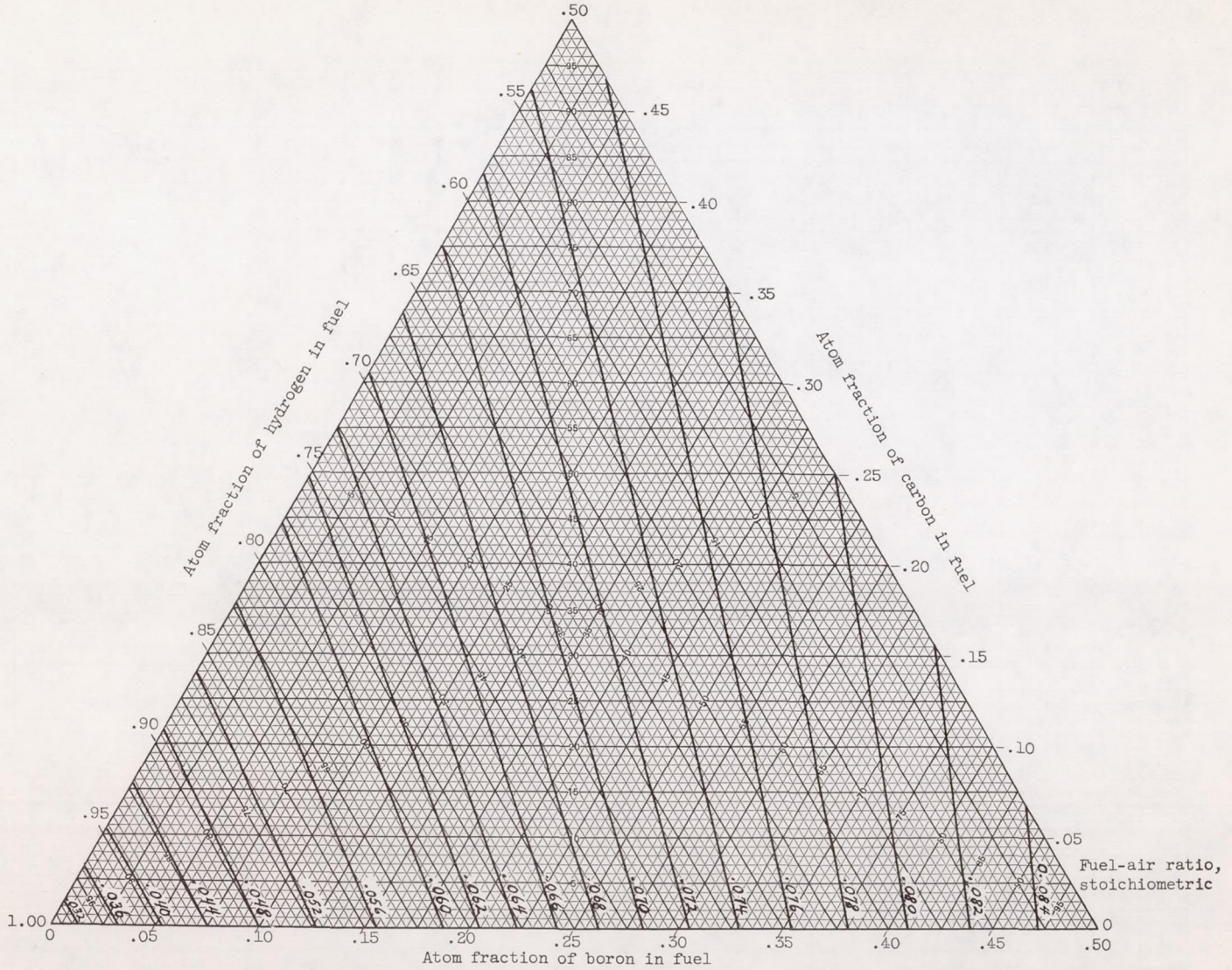


Figure 3. - Stoichiometric fuel-air ratio for fuel containing boron, carbon, and hydrogen.

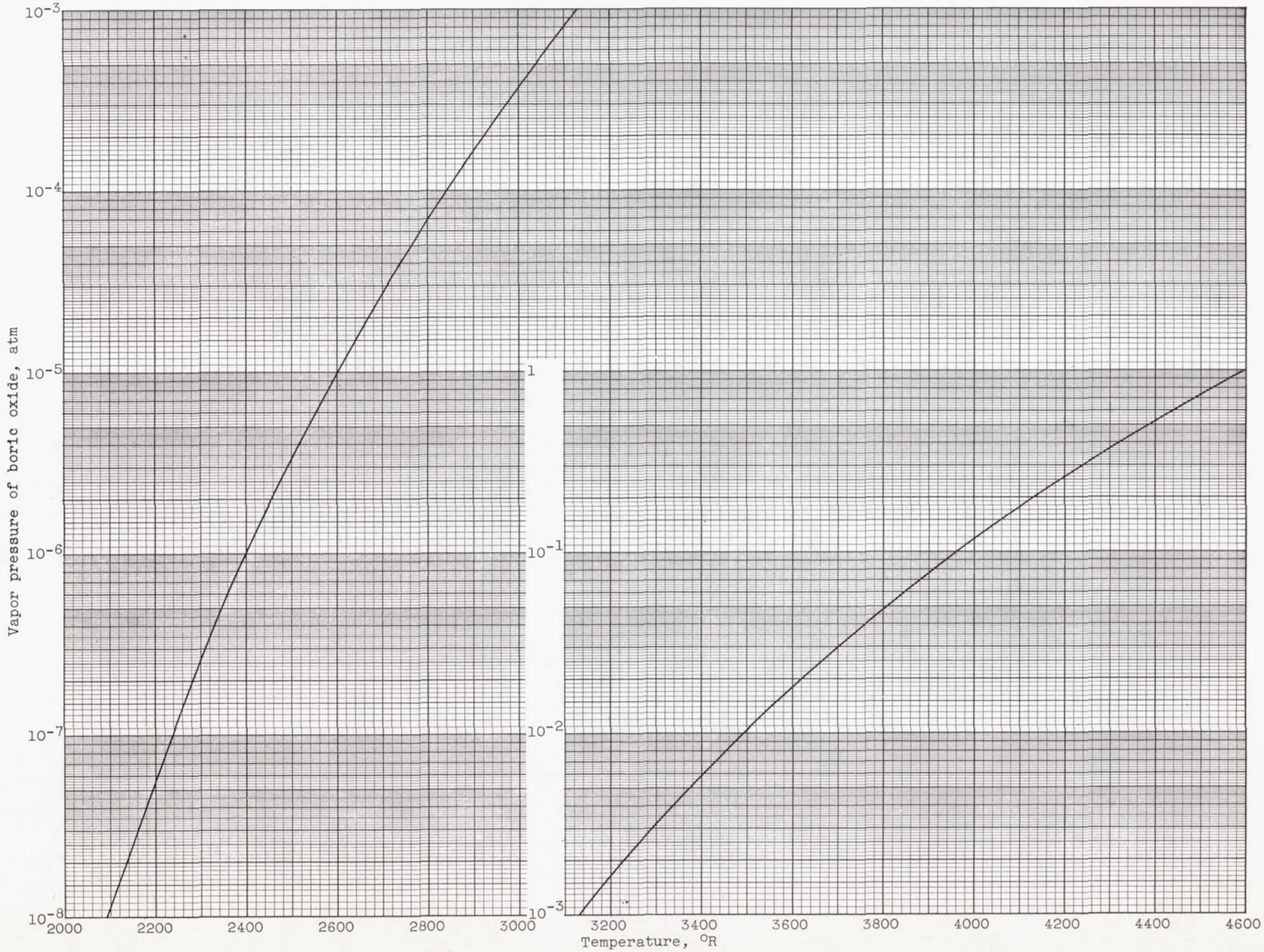
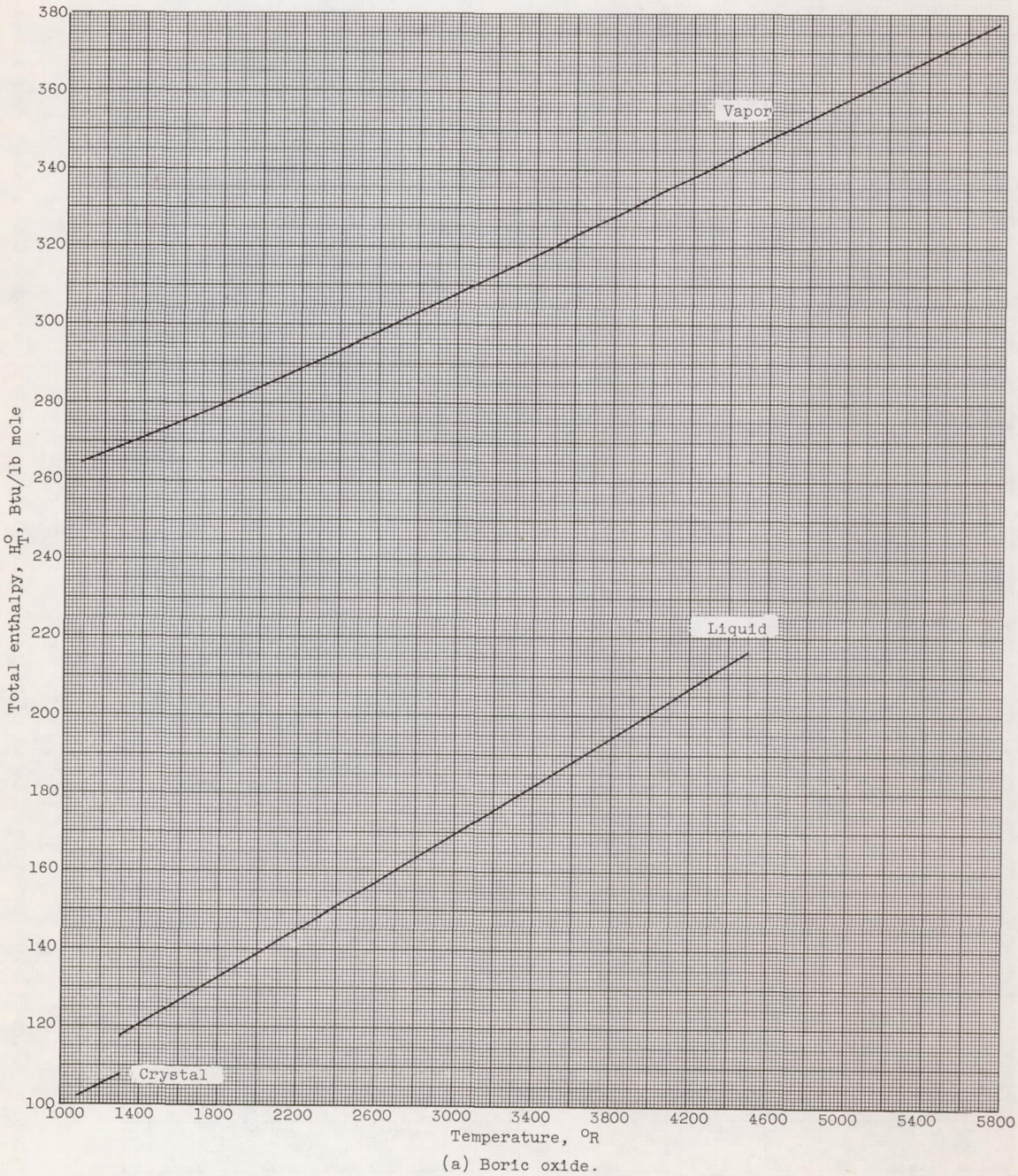


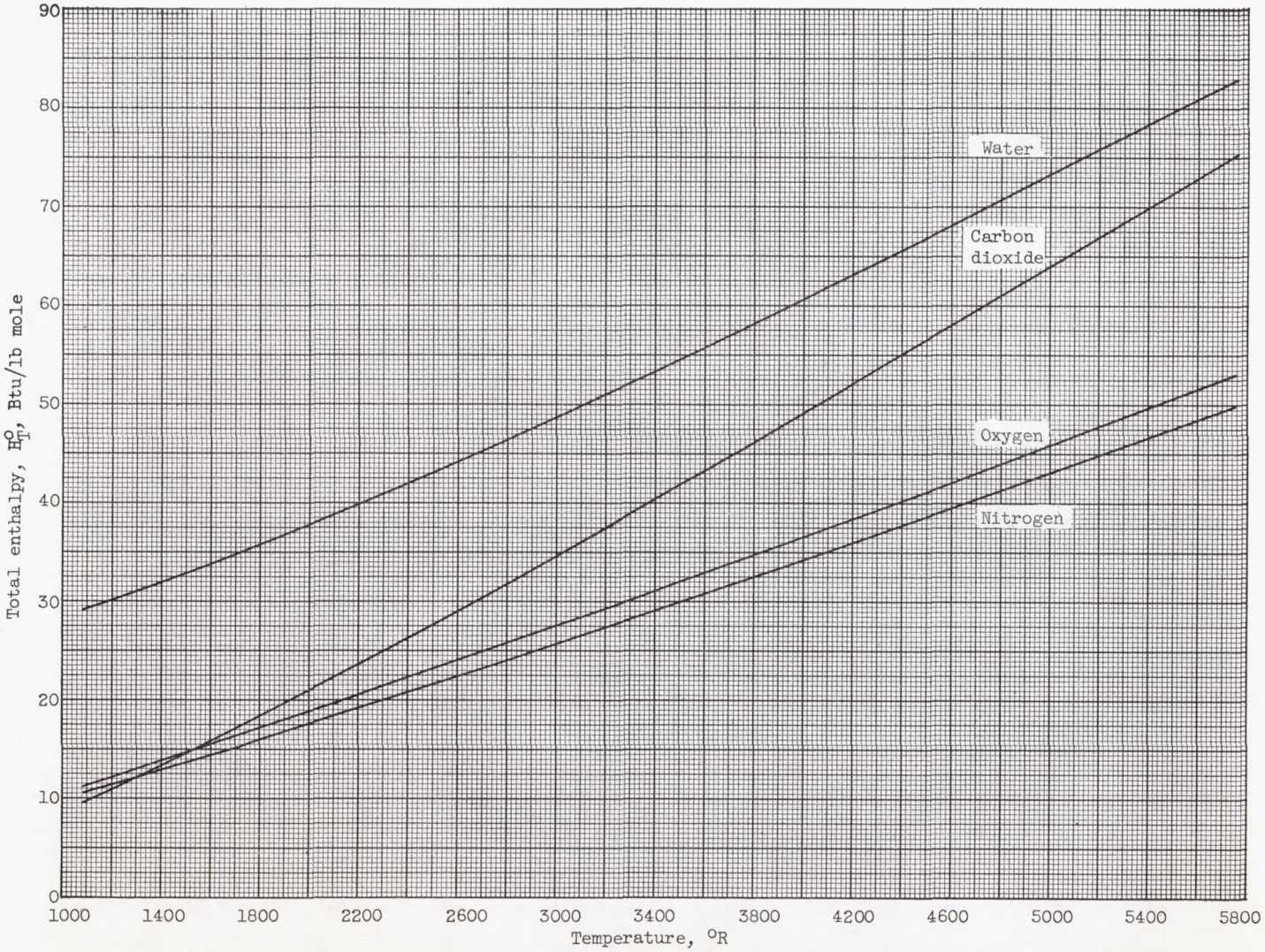
Figure 4. - Variation of boric oxide (B_2O_3) vapor pressure with temperature. (Data from ref. 6.)

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(a) Boric oxide.

Figure 5. - Variation of total enthalpy per mole with temperature for combustion-product constituents.



(b) Water, carbon dioxide, oxygen, and nitrogen.

Figure 5. - Concluded. Variation of total enthalpy per mole with temperature for combustion-product constituents.

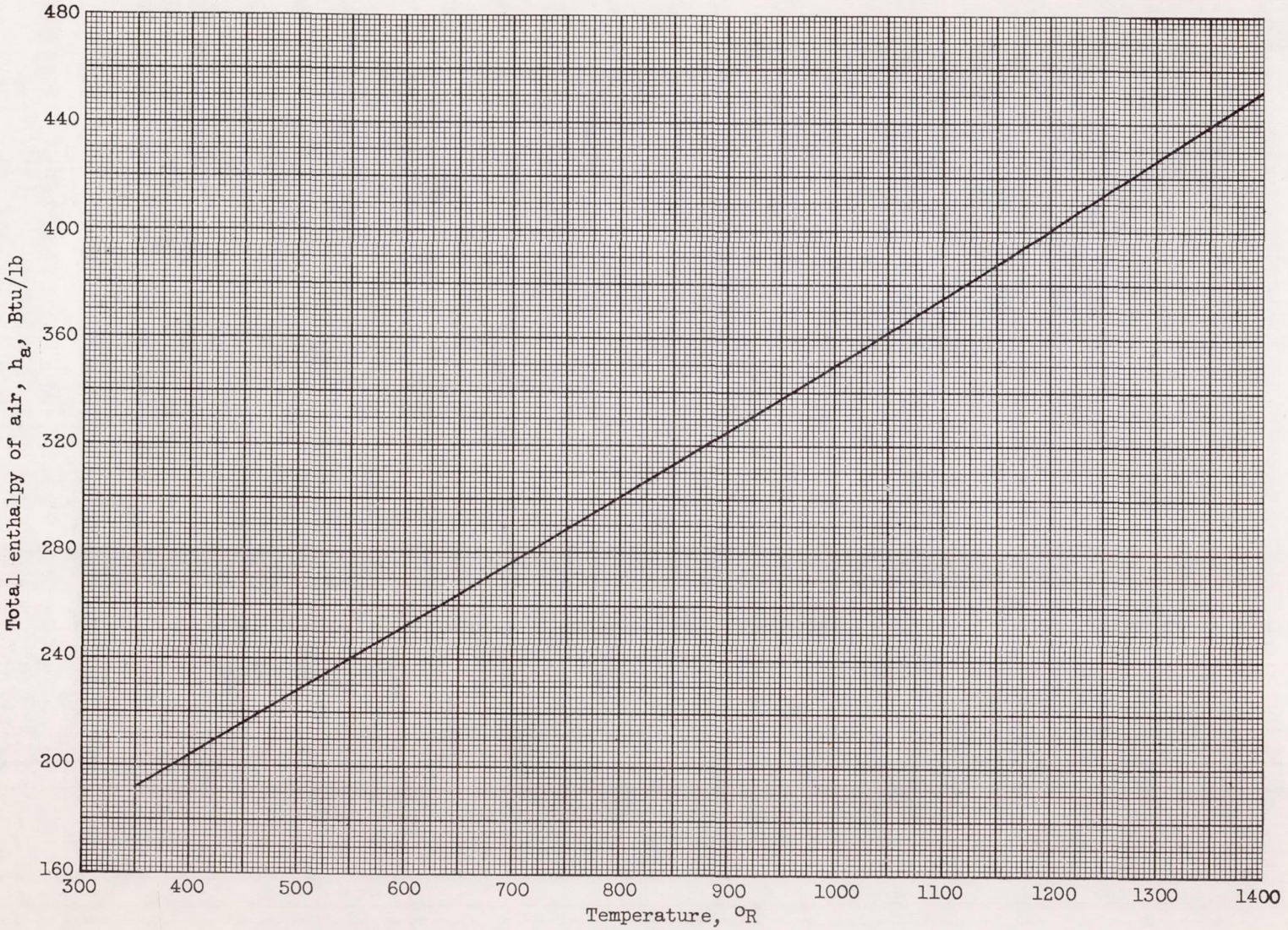


Figure 6. - Variation of total enthalpy of air with temperature.

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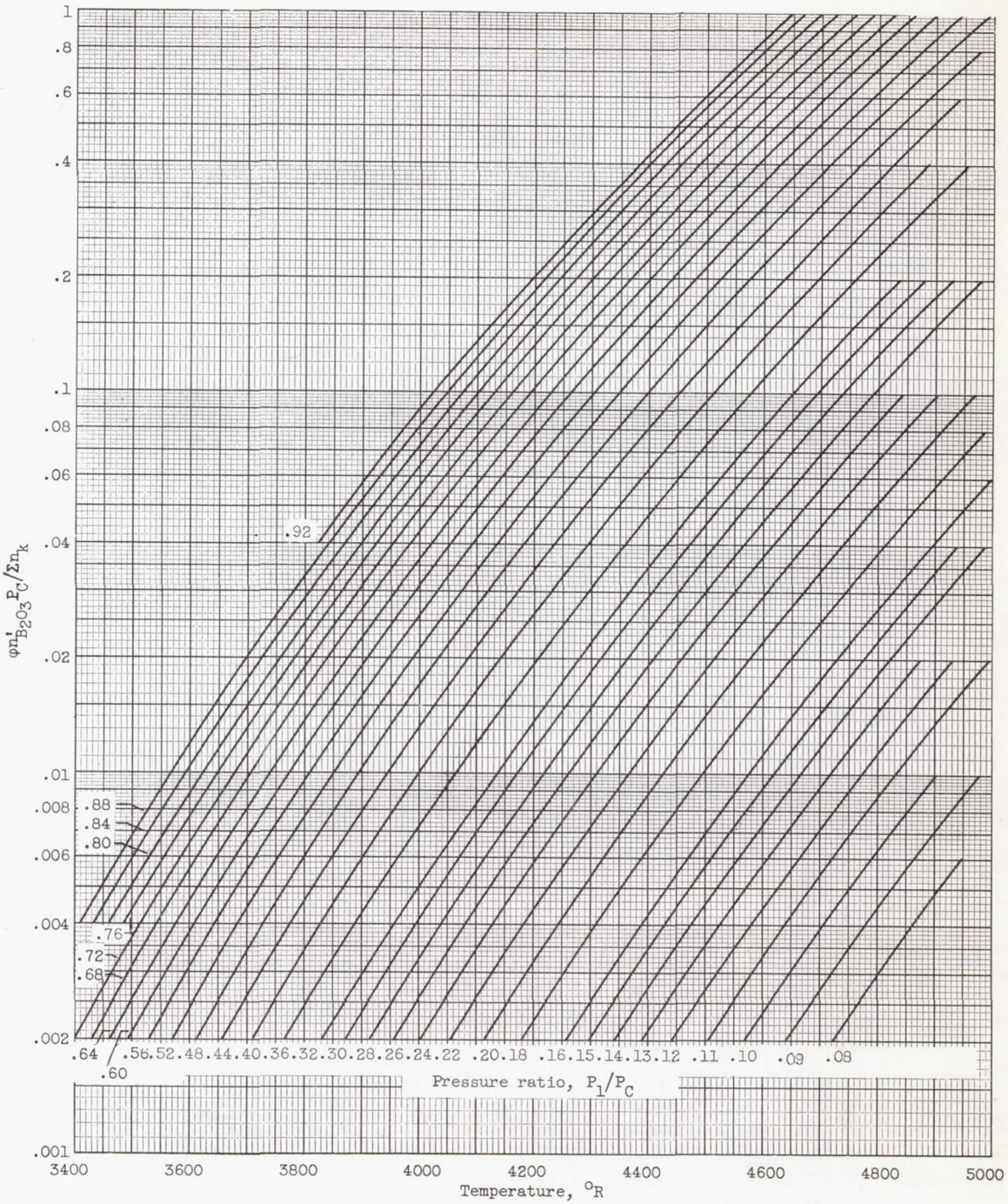
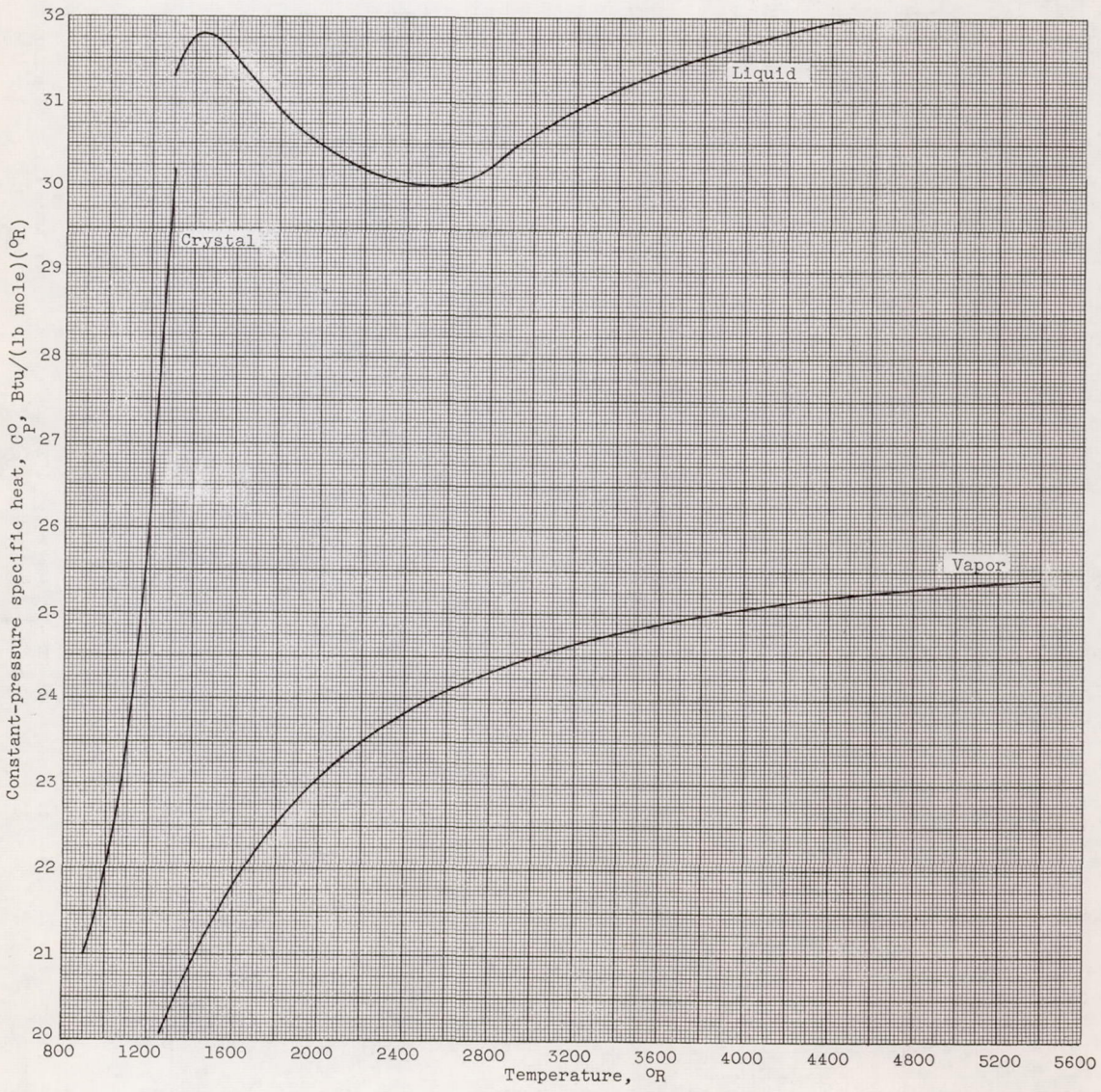


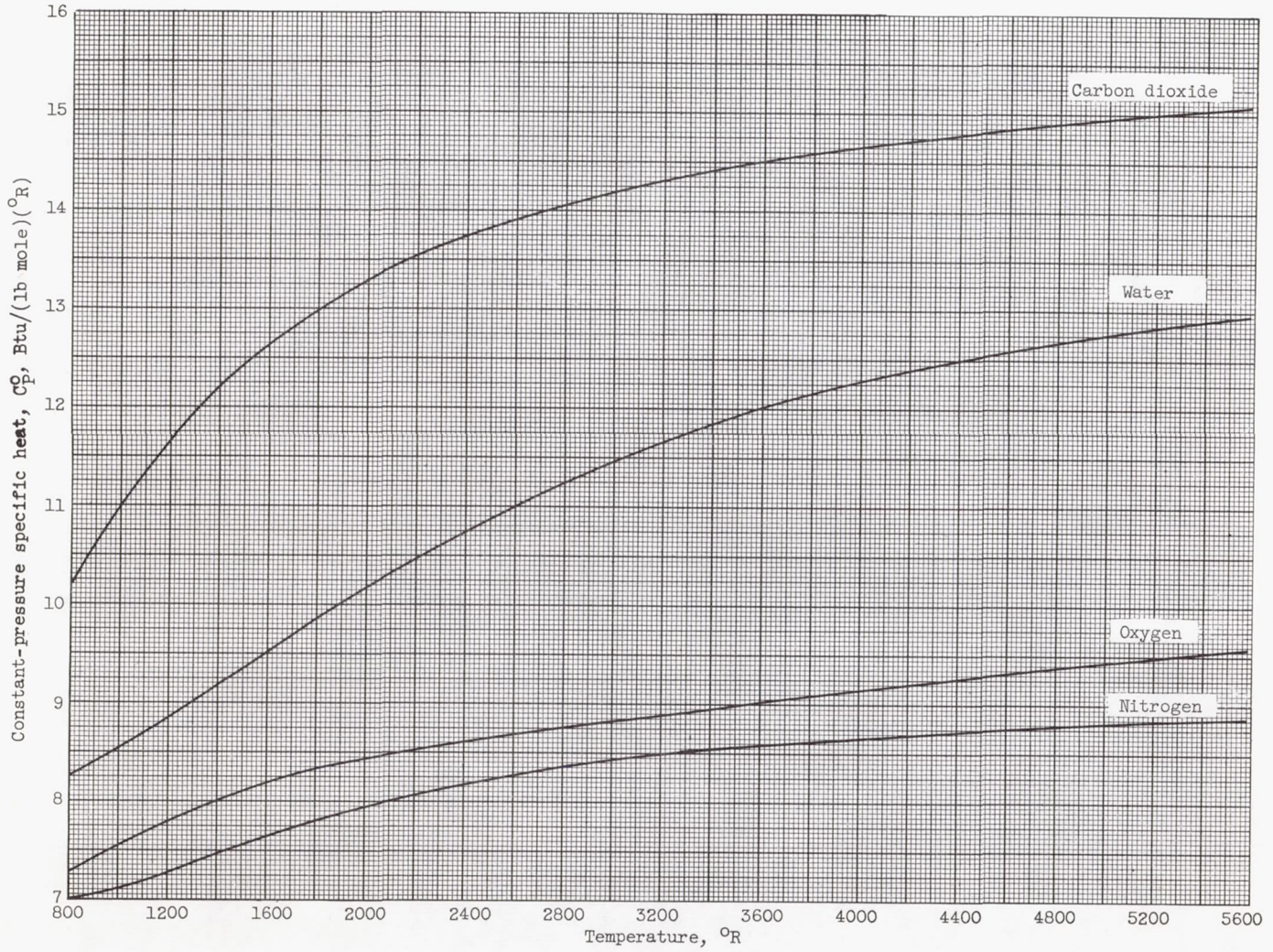
Figure 7. - Chart for determining conditions at saturation temperature from known combustor outlet conditions.

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(a) Boric oxide.

Figure 8. - Variation of molar constant-pressure specific heat with temperature for combustion-product constituents.



(b) Carbon dioxide, water, oxygen, and nitrogen.

Figure 8. - Concluded. Variation of molar constant-pressure specific heat with temperature for combustion-product constituents.

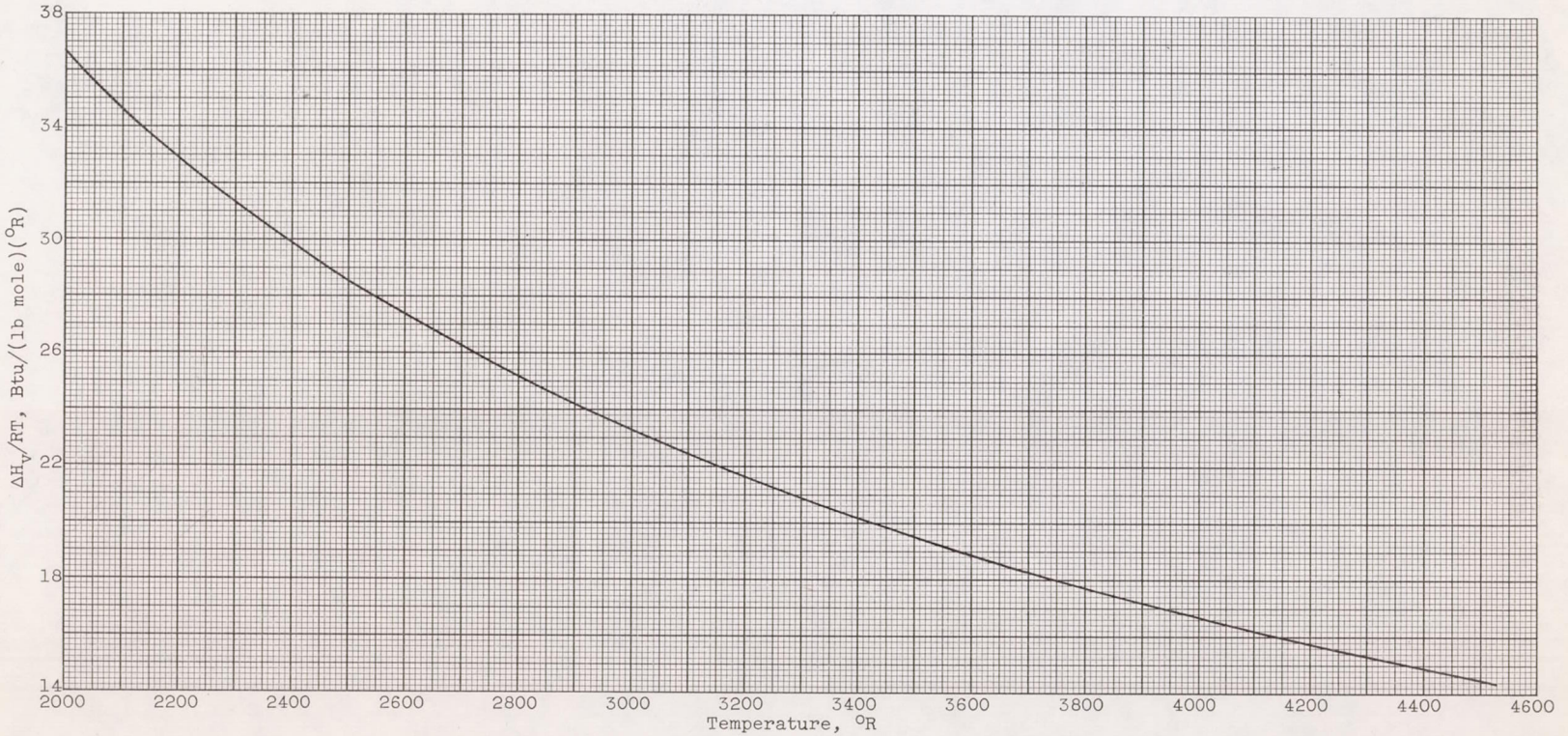


Figure 9. - Variation of $\Delta H_v/RT$ with temperature for boric oxide.